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THE AFTER-EFFECT OF HYDROSTATIC PRESSURE ON THE COLOR CENTERS IN ALKALI HALIDES*

BY RYO KIYAMA AND KIYOSHI SHIMIZU

Introduction

The authors reported in the previous papers^{1,2)} on the after-effect of hydrostatic pressure on the color centers formed in alkali halides by exposure to RaBr_2 and by electrolysis. Now, the authors have investigated the after-effect of hydrostatic pressure on the formation of the R- and M-bands by exposure to F- light for NaCl crystal colored by γ -ray irradiation from the source of Co^{60} and KCl, KBr and KI crystals colored by electrolysis, and confirmed the shift of the band peaks after the compression which was reported in the previous papers.

Experimentals

Preparation of samples The large single crystals used in this investigation were synthesized from the commercial reagents having the reagent proof by S. Kyropoulos' method. The specimens of each crystal were cleaved in size of $3.6 \times 6 \times 13 \text{ mm}$ for NaCl and of $5 \times 8 \times 13 \text{ mm}$ for KCl, KBr and KI from the same crystal blocks.

Procedure In order to investigate the after-effect of hydrostatic pressure on the formation of the R- and M-bands by the exposure to the F- light and on the position of the peak of absorption bands, the comparison between the compressed colored sample and that of one atmospheric pressure was performed.

The coloration of NaCl specimens was performed by the irradiation with γ -ray from radioactive Co^{60} . The NaCl specimens were exposed at the interval of 20 mm from the γ -ray source (20 mm curie) in the dark at room temperature for 67 days. The coloration of KCl, KBr and KI specimens was performed by the electrolysis with a pointed cathode of nichrome and a flat anode of platinum at elevated temperatures ($550^\circ \sim 700^\circ \text{C}$) and after coloration the colored specimen was rapidly quenched in the dark. Two pieces of

* This investigation has been done by K. Shimizu, being in the postgraduate course, under the direction of Prof. R. Kiyama.

1) S. Minomura, *This Journal*, 24, 28 (1954)

2) R. Kiyama, S. Minomura and M. Ōura, *Proc. Japan Acad.*, 30, 764 (1954)

the sample containing the nearly equal concentration of F-center were cleaved for the spectral measurement in size of about $1.4 \times 5 \times 13$ mm from the central colored region of the specimen.

V-center was produced in KI specimens by electrolysis at 550° and 600°C with a flat cathode and a pointed anode of platinum.

In order to increase or develop the R- and M-bands the colored samples were exposed to the F-light (NaCl, $460\text{ m}\mu$ for 5 minutes; KCl, KBr and KI, $558\text{ m}\mu$, $625\text{ m}\mu$ and $685\text{ m}\mu$ for 20 minutes respectively) by means of the Beckman model D U Quartz Spectrophotometer.

The compression of the samples was performed at $10,000\text{ kg/cm}^2$ for 24 hours (NaCl) and $7,500\text{ kg/cm}^2$ for 48 hours (KCl, KBr and KI) in mobil oil at room temperature by the ultra high pressure apparatus³⁾. After compression, the oil on the surface of the samples was washed down with petroleum ether.

The absorbance of the colored samples, $\log_{10}(I_0/I)$, where I_0 is the light transmitted through the non-colored sample and I is the light transmitted through the colored sample, was measured against the wavelengths at the interval of 5 or $10\text{ m}\mu$ in the vicinity of the peak of the absorption band and at the interval of $20\text{ m}\mu$ in the other region. The position of the peak of the absorption band was determined by extrapolation of the straight line on the mid-points of the band width.

Results

Increase of the R- and M-bands The absorption spectra of the compressed colored sample and the colored sample of one atmospheric pressure of four alkali halides (NaCl, KCl, KBr and KI) before and after the exposure to the F-light are shown by curves 1, 3 (compressed) and curves 2, 4

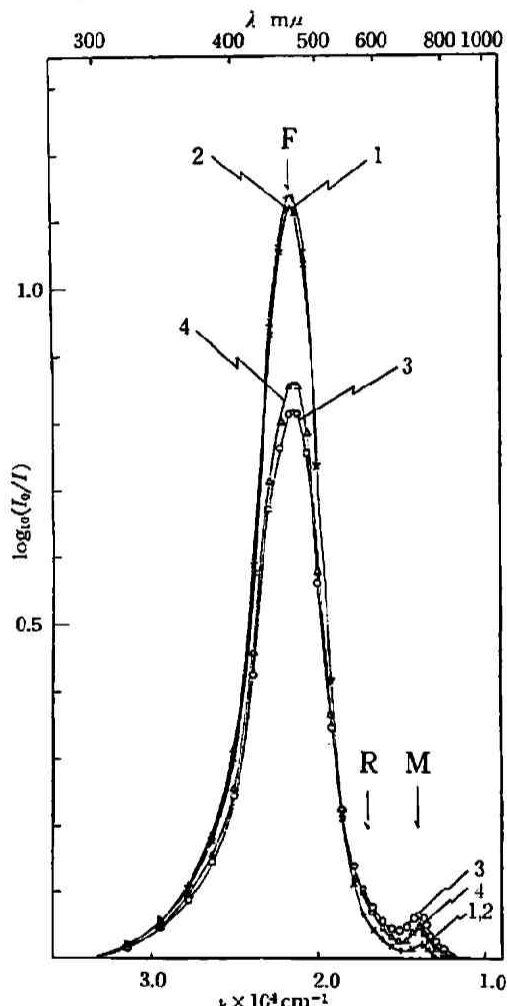


Fig. 1 Absorption spectra of NaCl before and after the exposure to the F-light

curve 1	before exposure	$10,000\text{ kg/cm}^2$
3	after "	
curve 2	before exposure	1 atm
4	after "	

3) R. Kiyama and S. Minomura, *This Journal*, 22, 49 (1952)

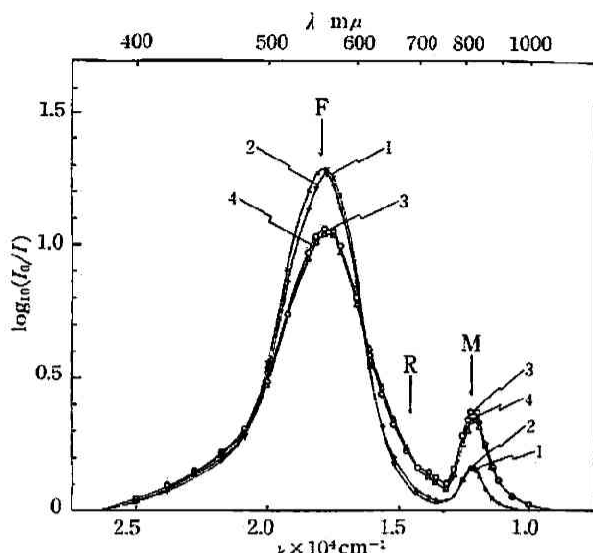


Fig. 2 Absorption spectra of KCl before and after the exposure to the F-light (Temp. of electrolysis, 600°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

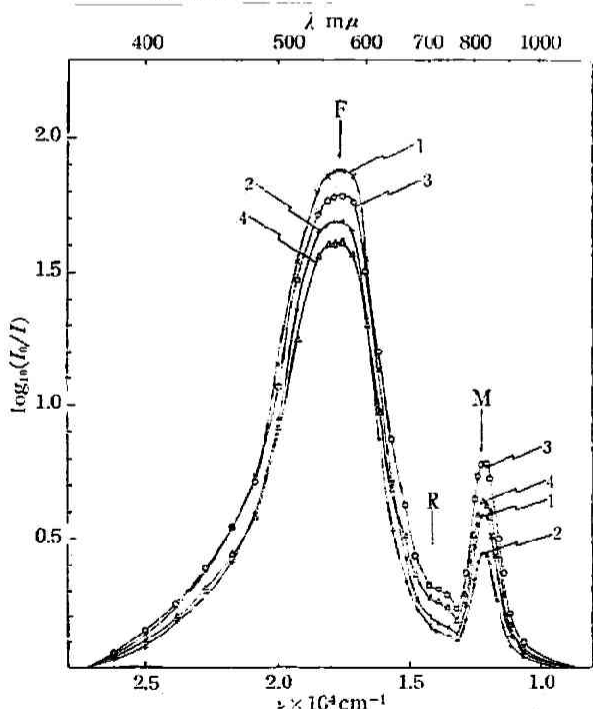


Fig. 3 Absorption spectra of KCl before and after the exposure to the F-light (Temp. of electrolysis, 700°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

(1 atm) in Figs. 1~7. Each figure shows that the F-band decreases with the F-light exposure and the M-band increases (Figs. 1, 2, 3 and 7) or generates (Figs. 4, 5 and 6). The agreement of the peak wavelength of both bands with those listed by Ivey⁴⁾ is reasonably satisfactory. At the same time, the absorption bands corresponding to the R-bands^{4,5)} increase over the region of wavelength between the F- and M-bands. In the case of KI, it is found that the weak absorption band increases in the short wavelength tail of the F-band with the F-light exposure.

The effect of temperature of electrolysis is as follows. Before the F-light exposure, the M-band is produced in KCl at 600° and 700°C and its absorbance increases with increasing temperature of electrolysis (curves 2 in Figs. 2 and 3). In KI, the M-band is produced at 650°C (curve 2 in Fig. 7), but at 550°C it can not be observed (curve 2 in Fig. 6). In KBr, the M-band is not produced at 600° and 700°C (curves 2 in Figs. 4 and 5). By the F-light exposure, the ratio of the increment of the integrated absorption ($\Delta \int \log_{10}(I_0/I) d\nu \text{ cm}^{-1}$) in R- and M-bands (in KI, the sum of increment of the R- and M-bands) to the decrement of the integrated absorp-

4) H. Ivey, *Phys. Rev.*, **72**, 341 (1947)

5) P. Pringsheim, *J. Chem. Phys.*, **18**, 1564 (1954)

tion in the F-band shows higher value with increasing temperature of electrolysis (curves 2 and 4 in Figs. 2~7, *cf.* Table).

The effect of high pressure is as follows. It is shown by comparing curves 1 and 3 (compressed) with curves 2 and 4 (1atm) in each figure that the ratio of the increment of the R- and M-bands to the decrement of the F-band in the compressed sample by the F-light exposure is larger than that in the sample of one atmospheric pressure (*cf.* Table). The fact that the rate of enhancement in the R- and M-bands by the F-light exposure becomes larger by applying the hydrostatic pressure to crystals or by quenching crystals from higher temperature, may be attributed to the facts that the internal strain is produced by such manipulation and the density of the lattice defects, especially the cluster of vacancies, is increased.

The shift of peaks of absorption band The peak wavelength of the F-band of compressed sample shifts to the shorter wavelength side by about $1\text{m}\mu$ in NaCl, $2\sim 3\text{m}\mu$ in KCl and KBr, and $1\sim 2\text{m}\mu$ in KI from that of the sample of one atmospheric pressure. In KCl, the peak wavelength of M-band of compressed sample shifts to the longer wavelength side by $\sim 2\text{m}\mu$ from that of the sample of one atmospheric pressure. In NaCl, KBr and KI, the absorbance of the M-band is, as shown in the figures, so low that the shift of peak can not be observed. In this experiment, the spectral measurement in the vicinity

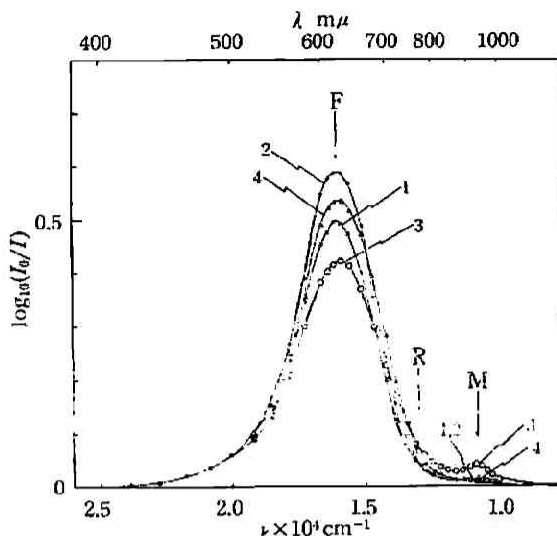


Fig. 4 Absorption spectra of KBr before and after the exposure to the F-light (Temp. of electrolysis, 600°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

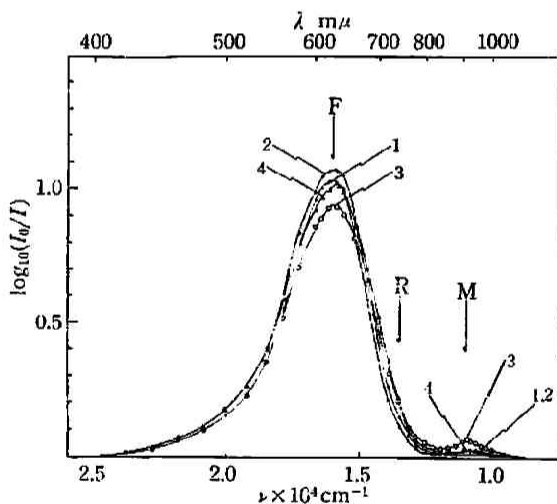


Fig. 5 Absorption spectra of KBr before and after the exposure to the F-light (Temp. of electrolysis, 700°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

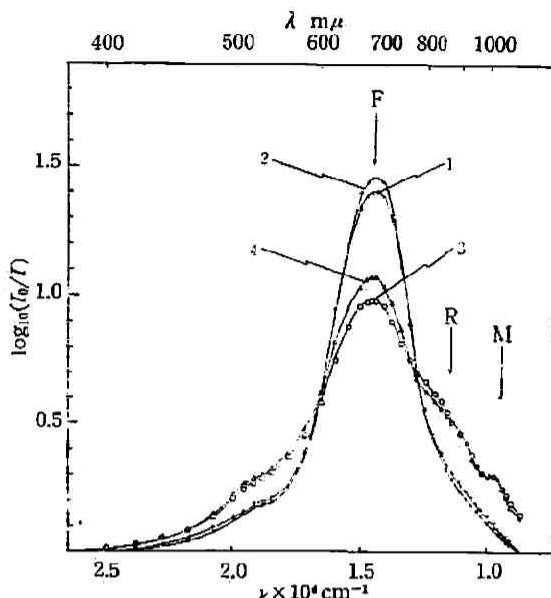


Fig. 6 Absorption spectra of KI before and after the exposure to the F-light (Temp. of electrolysis, 550°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

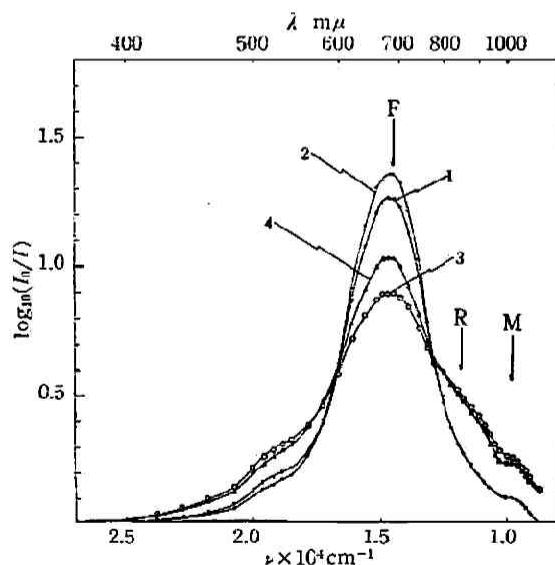


Fig. 7 Absorption spectra of KI before and after the exposure to the F-light (Temp. of electrolysis, 650°C)

curve 1	before exposure	7,500 kg/cm ²
3	after "	
curve 2	before exposure	1 atm
4	after "	

of the peak was performed at the interval of 10 mμ and the position of the peak was determined by extrapolation of the straight line on the mid-points of the band width, although in the previous papers the spectral measurement was performed at the interval of half grade of the wavelength notched in the spectrophotometer and the shifted position of the band peak was shown by the short wavelength edge of the flat peak which was caused by the overlapping of the absorption bands in the shifted and normal positions. Therefore, the quantity of the F-band obtained in this experiment results in smaller values in comparison with those in the previous papers^{1,2}.

The absorption spectra* of V-center produced in KI by electrolysis at 500° and 600°C are shown by curves 1 and 2 in Fig. 8. Two peaks which locate at 353 mμ or 355 mμ and about 290 mμ are shown in the V-band. The peak of the short wavelength side is indicated by the approximate wavelength because of no discrete structure. The peak wavelength of both peaks shows satisfactory agreement with Mollwo's data⁶). The peak of the band in the long wavelength side shifts from 353 mμ (550°C) to 355 mμ (600°C) with increasing temperature, but the shift of peak by compression (7,500 kg/cm², 48 hours) can not be observed.

* The measurement of this part was performed by Mr. M. Ōura.

6) E. Mollwo, *Ann. Phys.*, 29, 397 (1937)

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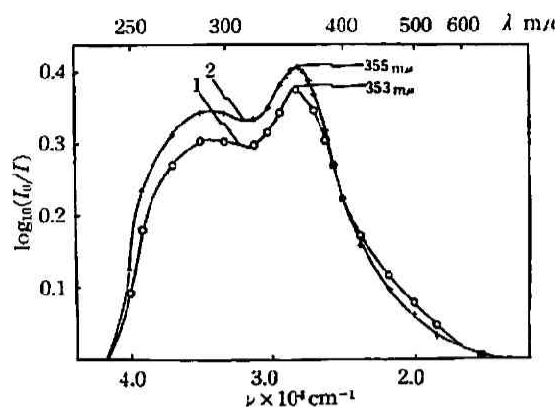


Fig. 8 Absorption spectra of V-band of KI
Temp. of electrolysis
curve 1: 550°C
curve 2: 600°C

Table Pressure effect on the variation of F-, R- and M-centers' absorption,
 $\mp \Delta f_{10}(I_0/I)d\nu \text{ cm}^{-1}$, by the exposure to the F-light

NaCl					
Band	$-\Delta F$	ΔM	ΔR	$\Delta M/-\Delta F\%$	$\Delta R/-\Delta F\%$
Pressure					
1 atm	11.9	0.57	0.89	4.8	7.5
10,000 kg/cm ²	12.2	1.09	1.02	8.9	8.4

KCl										
Band	600°C					700°C				
	$-\Delta F$	ΔM	ΔR	$\Delta M/-\Delta F\%$	$\Delta R/-\Delta F\%$	$-\Delta F$	ΔM	ΔR	$\Delta M/-\Delta F\%$	$\Delta R/-\Delta F\%$
Pressure										
1 atm	5.6	3.5	2.5	62.5	44.6	3.5	4.1	3.5	117	100
7,500 kg/cm ²	6.4	4.4	2.9	68.8	45.3	3.7	4.5	3.8	122	103

KBr										
Band	600°C					700°C				
	$-\Delta F$	ΔM	ΔR	$\Delta M/-\Delta F\%$	$\Delta R/-\Delta F\%$	$-\Delta F$	ΔM	ΔR	$\Delta M/-\Delta F\%$	$\Delta R/-\Delta F\%$
Pressure										
1 atm	1.4	0.054	0.60	3.9	42.9	1.7	0.27	1.5	15.9	88.9
7,500 kg/cm ²	1.7	0.42	0.92	24.7	54.1	2.0	0.69	1.8	34.5	90.0

KI						
Band	550°C			650°C		
	$-\Delta F$	$\Delta M+\Delta R$	$\Delta(M+R)/-\Delta F\%$	$-\Delta F$	$\Delta M+\Delta R$	$\Delta(M+R)/-\Delta F\%$
Pressure						
1 atm	9.6	6.4	66.7	8.1	6.5	80.3
7,500 kg/cm ²	10.9	8.0	73.4	8.9	7.3	82.0

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